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Quantitative Analysis of Polynuclear Aromatic Hydrocarbons in Liquid Fuels

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Quantitative Analysis of Polynuclear Aromatic Hydrocarbons in Liquid Fuels

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16. ABSTRACT

Polynuclear aromatic hydrocarbons (PNAs), formed in combustion processes with liquid hydrocarbon fuels, contribute to mobile source exhaust emissions. Because correlation between PNA levels in automobile exhaust and pre-existent PNAs in fuel has been demonstrated in previous work, a quantitative analysis of 12 individual polynuclear aromatic hydrocarbons present in various aircraft turbine, diesel, and gasoline test fuels was determined in this project. The PNAs included phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, triphenylene, benzo(a)pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, coronene and anthanthrene. The fuel samples were analyzed by combined gas chromatography/mass spectrometry (GC-MS) after a preliminary isolation/concentration scheme. Liquid crystal chromatographic columns were employed to resolve isomeric PNAs. The results indicated that anthanthrene and coronene were not detected in any of the samples analyzed. Although the detection limit for each PNA in the samples varied, the detection limit of the method employed was approximately 5µg/gallon (1 ppb). The remaining ten PNAs were found in levels ranging from 6µg/gallon (1.6 ppb = benzo(e)pyrene) to 3.1g/gallon (810,000 ppb = phenanthrene) of fuel. In general, the concentration decreased with increasing molecular weight of the PNAs.

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QUANTITATIVE ANALYSIS

OF

POLYNUCLEAR AROMATIC HYDROCARBONS

IN LIQUID FUELS

by

Radian Corporation
8500 Shoal Creek Boulevard
Austin, Texas 78766

EPA Contract No. 68-02-2446

Project Officer
James N. Braddock
Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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ABSTRACT

Polynuclear aromatic hydrocarbons (PNA's), formed in combustion processes with liquid hydrocarbon fuels, contribute to mobile source exhaust emissions. Because correlation between PNA levels in automobile exhaust and pre-existent PNAs in fuel has been demonstrated in previous work, a quantitative analysis of 12 individual polynuclear aromatic hydrocarbons present in various aircraft turbine, diesel, and gasoline test fuels was determined in this project. The PNAs included phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, triphenylene, benzo(a)pyrene, benzo(e)pyrene, benzo(g,h,i)perylene, coronene and anthanthrene. The fuel samples were analyzed by combined gas chromatography/mass spectrometry (GC-MS) after a preliminary isolation/concentration scheme. Liquid crystal chromatographic columns were employed to resolve isomeric PNAs. The results indicated that anthanthrene and coronene were not detected in any of the samples analyzed. Although the detection limit for each PNA in the samples varied, the detection limit of the method employed was approximately 5μg/gallon (1 ppb). The remaining ten PNAs were found in levels ranging from 6μg/gallon (1.6 ppb = benzo(e)pyrene) to 3.1g/gallon (810,000 ppb = phenanthrene) of fuel. In general, the concentration decreased with increasing molecular weight of the PNAs.

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The Radian Staff included Dr. Donald D. Rosebrook as Program Manager and Ronald G. Oldham as Project Director. The GC-MS analyses were performed by Dr. P. H. Lin. Acknowledgment is also given to J. L. Parr and B. J. Mayfield who contributed significantly to the program.

SECTION 1

INTRODUCTION

In order to correlate polynuclear aromatic hydrocarbon (PNA) levels in combustion source exhaust emissions with the concentrations of PNAs in various liquid hydrocarbon fuels, the EPA contracted Radian Corporation to determine the concentration of twelve specified PNAs in various test fuels. The PNAs of interest include:

- Phenanthrene
- Anthracene
- Flouranthene
- Pyrene
- Benz(a)anthracene
- Chrysene
- Triphenylene
- Benzo(a)pyrene
- Benzo(e)pyrene
- Benzo(g,h,i)perylene
- Coronene
- Anthanthrene

The approach employed for the analysis of the specified PNAs in each sample was combined gas chromatography-mass spectrometry (GC-MS) with operation in the selected ion monitoring mode. A preliminary isolation/concentration scheme was employed to remove the PNAs from the hydrocarbon fuel matrix. Isomeric PNAs were chromatographically resolved by utilizing liquid crystal liquid phases.

A total of ten test fuels were analyzed during the program. Each fuel was analyzed in duplicate. Blank samples were also analyzed.

The report presents the results from these analyses and describes the procedures employed.

SECTION 2

RESULTS

The results from the analyses of the ten fuel samples are presented in Table 1. All samples were analyzed in duplicate, and the results shown are the average from the two determinations. The two Couch #5 samples (A and B) were submitted to Radian as blind duplicates. The pooled standard deviation of each compound was calculated by taking the square root of the average of all the standard deviations squared. (This number represents the best estimate of the variance between duplicate analyses for each compound.) These pooled standard deviations for the replicate pairs are summarized in Table 2. The absolute concentration of any compound should be within two statistical deviations of the measured concentration 95% of the time (95% confidence interval) and within one standard deviation 60% of the time. The data from the blind duplicate samples support these pooled standard deviations. The reported concentration of all but two compounds (phenanthrene and pyrene) are within one standard deviation of the mean concentration while these two are within two standard deviations. Complete PNA results are given in Appendix B. A detailed description of the various test fuels is provided in Appendix A.

Anthanthrene and coronene were not detected in any of the samples analyzed. Although the detection limit for each PNA in the samples varied, in general, the detection limit of the method employed was approximately 5µg/gallon (1 ppb). The remaining ten PNAs were found in levels ranging from 6µg/gallon (1.6 ppb) to 3.1g/gallon (810,000 ppb) of fuel. In general, the concentration decreased with increasing molecular weight of the PNAs.

Samples were received and analyzed in three groups ranging from two to six samples per group. A blank sample consisting of cyclohexane was analyzed in duplicate with each sample set. In one of the blank samples, the compounds phenanthrene and anthracene were detected at a concentration corresponding to 360µg/gallon (96 ppb) and 12µg/gallon (3.1 ppb) respectively. These levels were attributed to residual fuel in the glassware employed for the extraction of the fuel samples EM-238-F and EM-239-F. PNAs were not detected in any of the other blank samples analyzed.

All samples and cyclohexane blanks were spiked with 9-bromoanthracene, d_{10}-anthracene or indenopyrene in the range of 4 to 38µg/gallon (1 to 10 ppb) before extraction to measure recovery. Table 3 presents recovery data for the blanks and two fuels, Jet A Fuel - low sulfur and EM-240-F. The recovery for the other samples could not be measured because of positive interference. The average percent recovery was found to be 94.6% and the standard deviation on individual recoveries was 17.0%. This recovery data can be utilized as an indication of the variability of the analytical method. The spike compounds were chosen to be chemically similar to the PNAs of interest. The excellent recovery of the spike compounds indicates that the procedure employed did not result in any losses of the PNAs of interest.

TABLE 1. CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN LIQUID FUELS

Fuel Designation	Concentration, µg/gallon[1]											
	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Triphenylene	Benz(a) anthracene	Chrysene	Benzo(e) pyrene	Benzo(a) pyrene	Benzo(g,h,i) perylene	Anthanthrene	Coronene
Jet A Fuel, Low Sulfur	6,800	530	45	68	14	ND (<2)[2]	11	6	ND (<2)	ND (<2)	ND (<2)	ND (<2)
Jet A Fuel, High Sulfur	8,300	760	180	250	27	ND (<2)	12	43	ND (<2)	ND (<2)	ND (<2)	ND (<2)
EH-238-F	2,600,000	16,000	95,000	38,000	53,000	34,000	110,000	570	160	240	ND (<20)	ND (<20)
EH-239-F	1,300,000	38,000	49,000	30,000	17,000	13,000	16,000	290	260	110	ND (<20)	ND (<20)
EH-240-F	30,000	760	610	200	280	210	310	38	280	ND (<10)	ND (<20)	ND (<20)
EH-241-F	3,100,000	33,000	61,000	53,000	16,000	13,000	24,000	200	170	68	ND (<20)	ND (<20)
EH-242-F	800,000	6,400	20,000	7,600	6,100	2,300	5,300	64	76	ND (<10)	ND (<20)	ND (<20)
COUCH #2	2,000,000	11,000	76,000	120,000	42,000	28,000	53,000	680	330	1[illegible]	ND (<20)	ND (<20)
COUCH #5A	19,000	1,200	6,800	21,000	6,100	3,600	4,500	1,400	800	50	ND (<20)	ND (<20)
COUCH #5B	42,000	1,200	7,800	10,000	4,500	2,000	4,500	1,200	720	18	ND (<20)	ND (<20)

NOTES: [1] = Average from duplicate determination

[2] = ND(<X) - Not detected; X represents the detection limit for the compound in the sample analyzed.

TABLE 2. POOLED STANDARD DEVIATION FOR DUPLICATE ANALYSES

Compound	Number of Duplicate Pairs	Pooled Standard Deviation (%)
Phenanthrene	10	18.5
Fluoranthene	10	12.2
Benzo(e)pyrene	10	14.2
Pyrene	10	20.8
Benz(a)anthracene	8	20.9
Benzo(a)pyrene	8	25.3
Anthracene	10	37.1
Triphenylene	10	35.5
Chrysene	10	35.3
Benzo(g,h,i)perylene	6	33.3

TABLE 3. RECOVERY OF SPIKED COMPOUNDS

Compound Spiked	Spiked Concentration, ppb	Sample Type	Amount Recovered, ppb	Percent Recovered
d_{10}-Anthracene	10.	Jet A Fuel, Low Sulfur	7.4	74
d_{10}-Anthracene	10.	Jet A Fuel, Low Sulfur	9.6	96
9-Bromoanthracene	10.	Blank	10.8	108
9-Bromoanthracene	10.	Blank	9.0	90
9-Bromoanthracene	10.	EM-240-F	11.5	115
9-Bromoanthracene	10.	EM-240-F	10.6	106
9-Bromoanthracene	1.02	Blank	0.71	70
9-Bromoanthracene	1.02	Blank	0.74	78
Indeno(1,2,3- c,d)pyrene	1.12	Blank	1.02	91
Indeno(1,2,3- c,d)pyrene	1.12	Blank	1.33	118

SECTION 3

DISCUSSION

EXPERIMENTAL

This program required the development and application of a multi-step procedure to measure PNAs at the low ppb level in liquid fuels. The approach that was utilized contained the following elements:

- isolation and concentration of the PNAs from the bulk sample matrix by liquid-liquid extraction,
- identification of the specified PNAs by GC-MS, and
- quantification of identified PNAs by GC-MS.

Isolation and Concentration of PNAs From Liquid Fuels

An extraction scheme was developed to isolate and concentrate the PNAs present in the liquid fuels. The procedure employed was a modification of the method described by Matsushita (1972) and is illustrated in Figure 1. The fuel sample (500 ml) was extracted three times with 300 ml of dimethylsulfoxide (DMSO). An equal volume of cold 20% HCl was then added to the combined DMSO extracts. The resulting DMSO-HCl mixture was extracted three times with 900 ml of cyclohexane. The cyclohexane extracts were combined and washed successively first with 200 ml of 5% sodium hydroxide followed by two 200 ml portions of distilled water. This extract was then concentrated by removal of the cyclohexane by distillation. The extract was placed in a round bottom flask in a heating mantle. A three-ball Snyder column was placed on top of the flask as a distillation column. Distillation was conducted at atmospheric pressure until all cyclohexane had been removed.

Initially, it was anticipated that a large concentration factor (500-1000) would be required in order to achieve the desired sensitivity (1µg/gallon). Therefore, it was anticipated that 500 ml of sample would be extracted and the solvent concentrated to 1 ml. With this procedure, PNAs at one microgram per gallon in the fuel would be at a concentration of 130 ng/ml in the concentrated extract.

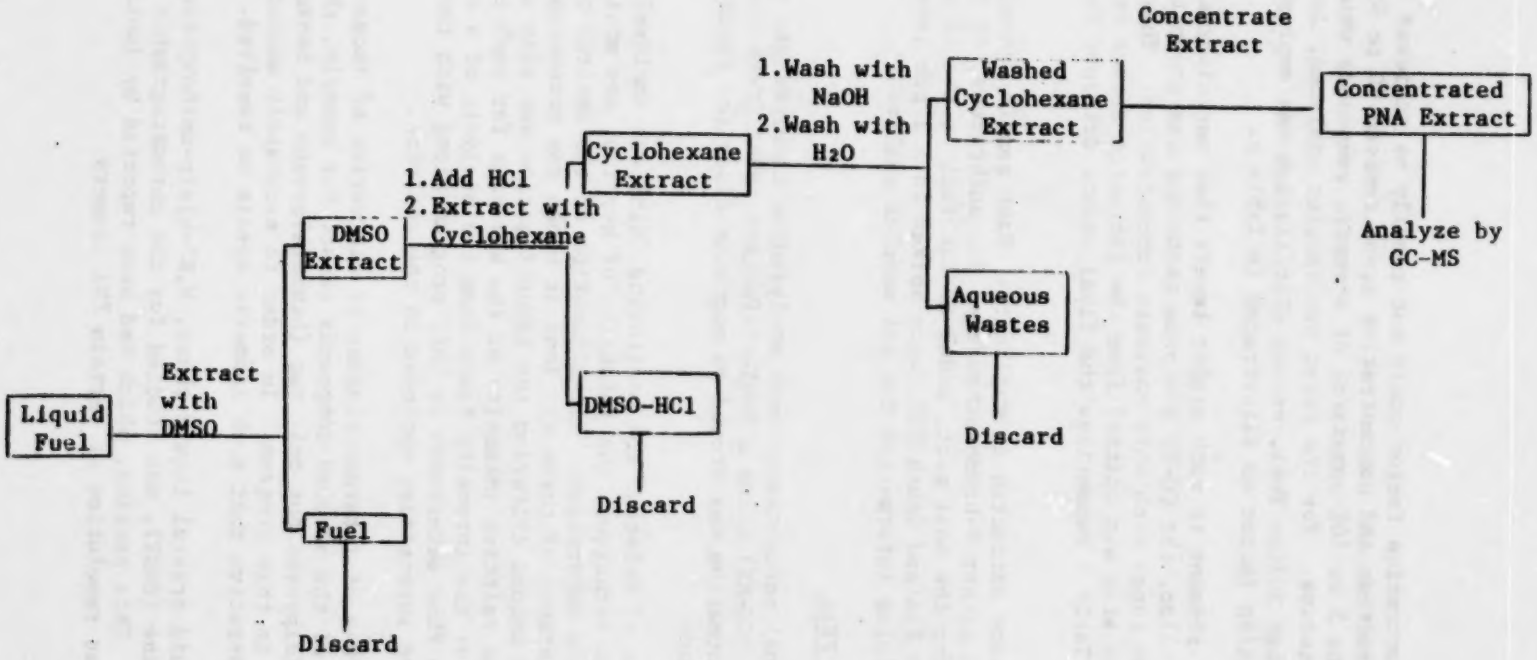


FIGURE 1. ISOLATION AND CONCENTRATION SCHEME FOR PNAs IN LIQUID FUELS

However, this concentration factor could not readily be achieved in the samples. Typically, the extraction and concentration steps removed 90 to 95% of the fuel. The remaining 5 to 10% consisted of aromatic compounds which were not removed by the procedure. For the first two samples analyzed, Jet A Fuel-Low Sulfur and Jet A-High Sulfur Fuel, vacuum distillation was employed to provide a higher concentration factor as illustrated in Table 4.

The PNAs were present in much higher levels than anticipated, frequently in the ppm range. Also, the GC-MS analysis technique was shown to be sensitive to the low ppb range with only moderate concentration. Therefore, the vacuum distillation step was omitted from the isolation scheme for the remaining samples. Table 4 summarizes the final volume obtained for each extract.

All samples were extracted in duplicate. Each sample was spiked prior to extraction with either 9-bromoanthracene, d_{10}-anthracene, or indenopyrene. The spikes were, for the most part, added to the fuel to the 10 ppb level. Two samples, Couch #5A and Couch #5B, were spiked to a 1 ppb level. Table 4 summarizes the spiking information for all samples analyzed.

Identification of PNAs

The liquid fuel concentrates were analyzed by combined gas chromatography/mass spectrometry (GC-MS) using a Hewlett-Packard 5982A GC-MS system. The mass spectral information was stored on magnetic discs for future interpretation and reference.

The technique of selected ion monitoring (SIM) was employed for all analyses. In this technique, the intensity of key ions was monitored during the chromatographic separation. Identification of the desired compounds was based on the appearance of these key ions at known gas chromatographic retention times. A second criterion for identification was also employed during the analysis. The relative intensity of the key ions for each compound had to be within 20% of the intensity found from the analysis of a standard. Table 5 lists the PNAs determined in this program along with the key ions and their relative intensities employed in the analysis.

The twelve PNAs of interest consist of six series of isomers. Other isomeric species of the desired compounds exist. For example, there are six isomers of benzo(a)pyrene but only two (benzo(a)pyrene and benzo(e)pyrene) were of interest in this program. In order to accurately measure each compound, it was imperative that e ch isomeric specie be resolved.

A novel liquid crystal liquid phase, N,N'-bis(p-methoxy-benzylidene) α,α'-bi-p-toluidine (BMBT), was studied for the chromatographic separation of the PNA isomers. This packing, which had been reported by Janini (1975), provides excellent resolution of certain PNA isomers.

TABLE 4. SUMMARY OF EXTRACTION PROCEDURES FOR LIQUID FUEL SAMPLES

Sample Designation	Radian Sample Number	Date Extracted	Spike	Spiked (ppb) Concentration	Volume of Concentrate, ml[1]
Jet A Fuel - Low Sulfur	556-1	9/15/77	d_{10} Anthracene	10.0	35 (2.4)[2]
Jet A Fuel - Low Sulfur	556-2	9/15/77	d_{10} Anthracene	10.0	33 (2.3)[2]
Jet A - High Sulfur	557-1	9/15/77	d_{10} Anthracene	10.0	37 (1.0)[2]
Jet A - High Sulfur	557-2	9/15/77	d_{10} Anthracene	10.0	25 (1.3)[2]
EH-238-F	826-A	11/8/77	9-Bromoanthracene	10.0	53
EH-238-F	826-B	11/8/77	9-Bromoanthracene	10.0	51
EH-239-F	825-A	11/8/77	9-Bromoanthracene	10.0	41
EH-239-F	825-B	11/8/77	9-Bromoanthracene	10.0	44
EH-240-F	827-A	11/8/77	9-Bromoanthracene	10.0	32
EH-240-F	827-B	11/8/77	9-Bromoanthracene	10.0	32
EH-241-F	823-A	11/8/77	9-Bromoanthracene	10.0	61
EH-241-F	823-B	11/8/77	9-Bromoanthracene	10.0	63
EH-242-F	824-A	11/8/77	9-Bromoanthracene	10.0	25
EH-242-F	824-B	11/8/77	9-Bromoanthracene	10.0	24
Couch #2	828-A	11/8/77	9-Bromoanthracene	10.0	55 (2)[2]
Couch #2	828-B	11/8/77	9-Bromoanthracene	10.0	57
Couch #5A	1556-A	9/1/78	9-Bromoanthracene Indeno - Pyrene	1.01 1.12	55
Couch #5B	1557-B	9/1/78	9-Bromoanthracene Indeno - Pyrene	1.01 1.12	66

NOTE: [1] = Volume of extract after removal of cyclohexane; sample volume 500 ml
[2] = (x) Volume of extract after vacuum distillation indicating final concentration volume.

TABLE 5. KEY IONS FOR THE SIM ANALYSIS OF PNAs IN LIQUID FUELS

Compound	M_1	Relative Intensity	M_2	Relative Intensity	M_3	Relative Intensity
Phenanthrene	178	100%	89	17%	176	15%
Anthracene	178	100%	89	16%	176	15%
Fluoranthene	202	100%	101	23%	100	14%
Pyrene	202	100%	101	26%	100	17%
Benz(a)anthracene	228	100%	229	19%	226	19%
Triphenylene	228	100%	229	19%	226	23%
Chrysene	228	100%	229	19%	226	20%
Benzo(e)pyrene	252	100%	126	23%	250	16%
Benzo(a)pyrene	252	100%	126	23%	250	16%
Benzo(g,h,i)perylene	276	100%	138	37%	274	27%
Anthanthrene	276	100%	138	37%	274	27%
Coronene	300	100%	150	64%	149	46%

Two additional liquid crystals recently developed (Janini, 1976, Janini, 1976) were also studied. These liquid phases, N,N'-bis(p-butoxy-benzylidene) α,α'-bi-p-toluidine (BBBT) and N,N'-bis(p-phenyl-benzylidene) α,α'-bi-p-toluidine (BPhBT), also provided excellent separation of certain PNA isomers. These phases are commercially available from Supelco.

Each of the three liquid crystals have different characteristics. While both BBBT and BMBT are satisfactory for 3 to 7 ring PNAs, BBBT has less column bleed at elevated temperatures. Chromatographic resolution on liquid crystals is highly dependent on temperature, with the best resolution achieved with the liquid crystal in the nematic state. BMBT and BBBT are nematic in the temperature range of 190° to 300°C, while BPhBT is nematic in the temperature range of 260° to 400°C. Therefore, BPhBT is generally limited to 5-7 ring compounds becasue of its temperature range. Early in the study it was determined that slight variations in the temperature programming conditions could cause drastic changes in resolution. Because of this temperature dependence of the liquid crystals, it was very difficult to resolve all of the PNA isomers in one analysis as illustrated in Figure 2. Changes in the temperature programming will easily resolve either phenanthrene and anthracene (m/e 178) or chrysene, triphenylene and benz(a)anthracene (m/e 228). However, careful selection of the chromatographic conditions was required in order to separate all of these isomers in one analysis.

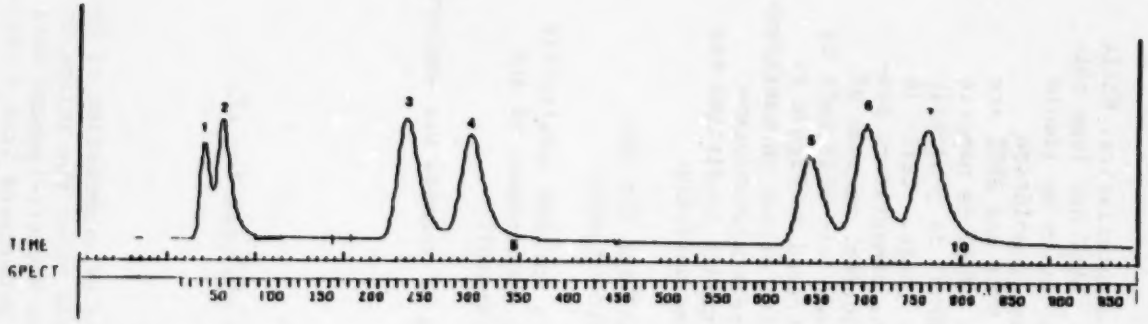
Therefore, it was decided to employ separate GC analyses for the different isomeric species. The benefits from this approach were:

- the instrument gain could be adjusted to obtain maximum sensitivity for the high molecular weight PNAs by allowing measurement of the more abundant low molecular weight species separately,
- the best chromatographic column for each group of isomers was employed, thus improving the separation,
- temperature control was not critical, and
- the overall analysis time was often shortened.

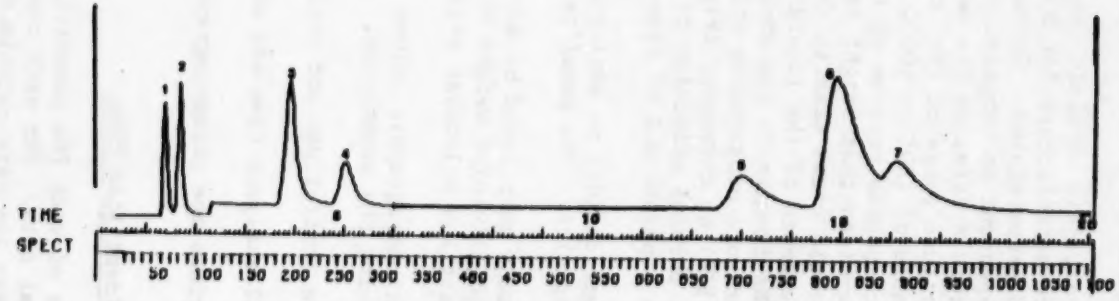
Table 6 summarizes the chromatographic conditions employed for all analyses.

Quantification of Identified PNAs

Quantification of each PNA identified was achieved by examination of the stored mass spectral data. For each compound, the areas under the intensity profiles for each key ion were calculated employing the Hewlett-Packard data system. The total mass of each compound injected was determined from a calibration curve. A typical calibration curve is shown in Figure 3. Each



GC Conditions: 240° for 4 minutes
then 8°/minute to 280°C



GC Conditions: 220° for 8 minutes
then 8°/minute to 290°C

FIGURE 2. SELECTED ION CHROMATOGRAMS FROM THE ANALYSIS OF A STANDARD PNA MIXTURE ON BBET AT TWO GC TEMPERATURE PROGRAMMING CONDITIONS

PNAs 1) Phenanthrene, 2) Anthracene, 3) Fluoranthene, 4) Pyrene, 5) Triphenylene
6) Benz(a)anthracene, 7) Chrysene

TABLE 6. GC-MS OPERATING CONDITIONS FOR LIQUID FUEL EXTRACTS

Column	Packing	Carrier Gas	Flow Rate (ml/min)	Initial Temperature (°C)	Initial Time (minutes)	Final Temperature (°C)	Program Rate (°C/min)	Samples Analyzed	Isomers Resolved
6' x ¼" glass	1.5% BBBT on 100/120 Supelcoport	He	30	200	4	280	8	Jet A Fuel, Low Sulfur Jet A Fuel, High Sulfur	All
6' x ¼" glass	1.5% BBBT on 100/120 Supelcoport	He	30	210	2	260	8	EM-238 EM-242 EM-239 Couch #2 EM-240 EM-241	Phenanthrene, Anthracene, Fluoranthrene, Pyrene, Chrysene, Benz(a)-anthracene, Triphenylene
6' x ¼" glass	2.5% BBBT on 100/120 Supelcoport	He	30	300	-	300	-	EM-338 EM-241 EM-239 EM-242 EM-240 Couch #2	Benzo(a)pyrene Benzo(e)pyrene
2 x ¼" glass	1.5% BPhBT on 100/120 Supelcoport	He	30	280	-	280	-	EM-438 EM-241 EM-239 EM-242 EM-24 Couch #2	Benzo(g,h,i)-perylene, Anthanthrene Coronene
6 x ¼" glass	5% SP-2100+ 1% BBBTm on 100/120 Supelcoport	He	30	200	0	260	8	Couch 5A Couch 5B	Phenanthrene, Anthracene Fluoranthrene Pyrene
6' x ¼" Glass	1.5% BPhBT on 100/120 Supelcoport	He	30	270	0	290	8	Couch 5A Couch 5B	Benz(a)anthracene Chrysene, Triphenylene Benzo(a)pyrene Benzo(e)pyrene
2' x ¼" glass	1.5% BPhBt on 100/120 Supelcoport	He	30	290	-	290	-	Couch 5A Couch 5B	Benzo(g,h,i)-perylene Anthracene Coronene

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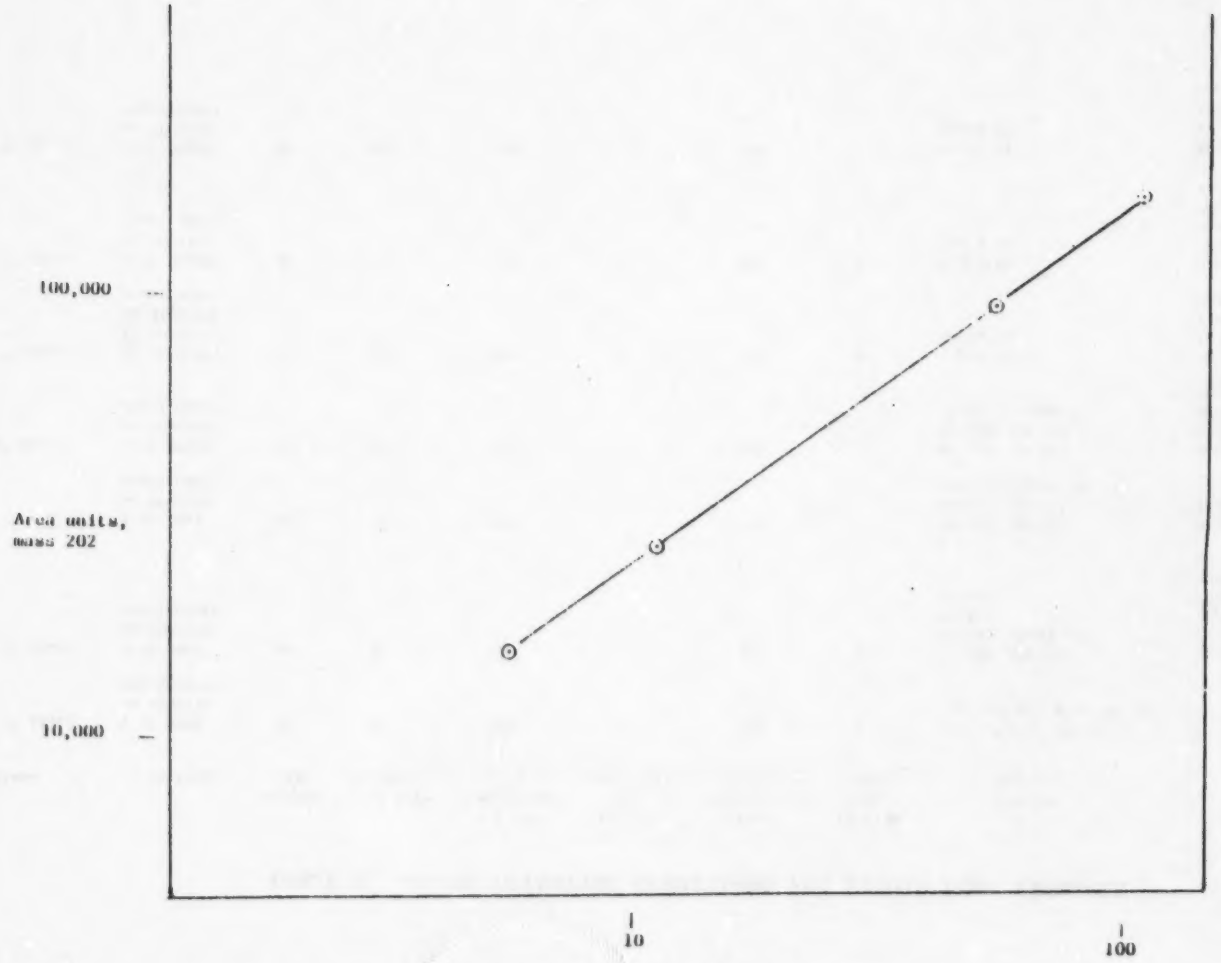

Figure 3. Typical Calibration Curve for Pyrene

calibration curve was generated by analyzing a series of at least four standards at varying concentrations. The concentration of each compound in the sample was then calculated according to the following equation:

$$ppb = \frac{\mu g \text{ PNA}}{\mu \ell \text{ injected}} \times \frac{m\ell \text{ concentrate}}{\ell \text{ sample extracted}}$$

The GC-MS-SIM technique employed is very sensitive with absolute lower detection limits on the order of 100 pg/µl injected for each compound. However, the detection limit for each compound is also dependent on the background (noise) of the ions measured. The detection limit, therefore, varied from sample to sample, depending on the sample matrix and instrumental conditions.

Interferences

Prior to liquid-liquid extraction, each sample was spiked at the low ppb level with selected compounds in order to demonstrate overall PNA recovery. Analysis of several of the sample concentrates by SIM GC-MS for the spiked component yielded data that corresponded to a recovery of >1000%. Further analysis of these sample extracts by repetitive scan GC-MS revealed that fragment and parent ions were present with significant intensity at virtually all masses below m/e 300. This unresolved background prevented the accurate measurement of the low level spiked compound in many of the sample extracts. However, in all sample extracts where the background was not present, excellent recovery of the spikes was demonstrated.

QUALITY CONTROL

The results from the quality control analyses (duplicate analyses and spikes) indicated that all analyses were conducted in a manner consistent with good analytical practice. Statistical tests were performed to determine whether the average of the variance of the percent recovered varied between low and high concentrations or between spikes in blank and spikes in actual samples. No statistically significant differences were observed.

A 95% confidence interval for the average percent recovered is 95.3± 12.49, or 83% to 108%. Therefore, there is no statistical evidence in a bias in the extraction/analysis procedures.

Ninety-two pairs of measurements were analyzed to determine the random variability of a single concentration determination. No evidence was found that the percent variability depended on concentration or chemical species.

RECOMMENDATIONS AND CONCLUSIONS

The analytical scheme developed during this program was successfully employed to determine the levels of the specified PNAs. The procedure requires the use of sophisticated instrumentation and skilled analysts.

Nevertheless, the advantages of specificity, sensitivity and accuracy are currently not realized by other analytical techniques.

The primary areas for improvement in the current analytical scheme are in the chromatography and the preliminary isolation scheme. Additional investigation into liquid crystals should continue to improve the separation of the various isomers. The combination of liquid crystals with traditional chromatographic phases should be of particular interest.

The isolation scheme employed successfully isolated the PNAs from the fuel matrix. However, other aromatic species were also carried through the separation scheme. Additional effort directed towards removal of these species should result in increased sensitivity.

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APPENDIX A

TEST FUEL DESCRIPTION

TABLE A-1. TEST FUEL DESCRIPTION

Test Fuel Designation	Type of Fuel	Where Used	Reference
Jet A High Sulfur	Aircraft turbine jet fuel	Commercial jet aircraft	Robertson, D. J., J. H. Elwood, and R. H. Groth, Chemical Composition of Exhaust Particles from Gas Turbine Engines. Final report prepared by United Technologies Corporation, East Hartford, Conn., under Contract No. 68-02-2450 to the U. S. Environmental Protection Agency, Research Triangle Park, NC Publication No. EPA-600/2-79-041, February 1979.
Jet A Low Sulfur	Aircraft turbine jet fuel		
EM-238-F	Diesel: No. 2-D smoke test fuel	Diesel-powered passenger cars and trucks.	Braddock, J. N., and P. A. Gabele, Emissions patterns of diesel-powered passenger cars - Part II. SAE Paper No. 770168 Detroit, February 1977.
EM-239-F	Diesel: National average No. 2 fuel.		
EM-240-F	Diesel: No. 1 Jet A fuel		Hare, C. T., and R. L. Bradow. Characterization of heavy-duty diesel gaseous and particulate emissions, and effects of fuel composition. SAE Paper No. 790490. Detroit, February 1979.

TABLE A-2. TEST FUEL DESCRIPTION

Test Fuel Designation	Type of Fuel	Where Used	Reference
EM-241-F	Diesel: Minimum Quality No. 2 fuel.	Diesel-powered cars and trucks	Braddock, J. N., and P. A. Gabele. Emissions patterns of diesel-powered passenger cars - Part II. SAE Paper No. 770168. Detroit 1977.
EM-242-F	Diesel: Premium Quality No. 2 fuel.		
Couch No. 2	Diesel: Local (Durham, NC) No. 2 fuel.		Hare, C. T., and R. L. Bradow, Characterization of heavy-duty diesel gaseous and particulate emissions and effects of fuel composition. SAE Paper No. 790490. Detroit, February 1979.
Couch 5A	Diesel: Local (Durham, NC) No. 2 fuel.		Hare, C. T., and T. M. Baines. Characterization of particulate and gaseous emissions from two diesel automobiles as a function of fuel and driving cycle. SAE Paper No. 790424. Detroit, February 1979.

TABLE A-3. TEST FUEL ANALYSES

Analysis	Jet A High Sulfur	Jet A Low Sulfur	EM-238-F	EM-239-F	EM-240-F
API Gravity @ 60°F	47.0	47.3	35.9	35.9	43.9
Density, gm/cc	0.792	0.791	0.845	0.844	0.804
ASTM Distillation, °F					
IBP	328	336	394	369	344
10%	338	344	424	428	362
50%	358	363	498	496	397
90%	403	410	600	576	458
EP	456	455	658	624	506
FIA Analysis					
% Saturates	80.0	79.1	74.5	82.4	83.1
% Olefins	1.5	1.6	0.3	0.4	2.4
% Aromatics	18.5	19.3	25.2	17.2	14.5
Cetane	----	----	48.6	48.7	47.4
Carbon, Weight %	----	----	83.6	83.12	83.98
Hydrogen, Weight %	----	----	14.72	14.96	14.86
Sulfur, Weight %	0.25	0.007	0.27	0.23	0.04

TABLE A-4. TEST FUEL ANALYSIS

Analysis	EM-241-F	EM-242-F	Couch No. 2	Couch No. 5A Couch No. 5B
API Gravity @ 60°F	32.4	38.7	34.6	35.5
Density, gm/cc				
ASTM Distillation, °F				
IBP	378	377	376	380
10%	425	417	418	427
50%	483	488	498	504
90%	570	572	590	600
EA	610	610	642	642
FIA Analysis				
% Saturates	59.8	81.6	68.9	66.2
% Olefins	0.5	0.4	1.5	1.3
% Aromatics	39.7	18.0	29.6	32.5
Cetane	41.8	53.0	46.0	----
Carbon, Weight %	84.36	84.00	84.62	84.59
Hydrogen, Weight %	13.95	14.98	14.80	14.81
Sulfur, Weight %	0.30	0.27	0.17	0.16

APPENDIX B

PNA ANALYSES OF LIQUID FUELS

TABLE B-1

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN JET A FUEL - HIGH SULFUR

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	2,700.	10,000.	1,800.	6,800.	2,200.	8,300.
Anthracene	250.	950.	150.	570.	200.	760.
Fluoranthene	45.	170.	50.	190.	48.	180.
Pyrene	64.	240.	87.	330.	76.	290.
Triphenylene	4.6	17.	9.9	37.	7.2	27.
Chrysene	3.0	11.	3.4	13.	3.2	12.
Benzo(e)pyrene	9.6	36.	13.3	50.	11.4	43.

TABLE B-2

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN JET A FUEL, LOW SULFUR

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	1,900.	7,200.	1,800.	6,800.	1,800.	6,800.
Anthracene	130.	490.	140.	530.	140.	530.
Fluoranthene	11.	42.	14.	53.	12.	45.
Pyrene	13.	49.	22.	83.	18.	68.
Triphenylene	1.8	6.8	5.3	20.	3.6	14.
Chrysene	3.2	12.	2.4	9.1	2.8	11.
Benzo(e)pyrene	1.4	5.3	1.9	7.2	1.6	6.1

TABLE B-3

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN EM-238-F

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	710,000.	2,700,000.	650,000.	2,500,000.	680,000.	2,600,000.
Anthracene	1,900.	7,200.	6,700.	25,000.	4,300.	16,000.
Fluoranthene	28,000.	110,000.	22,000.	83,000.	25,000.	95,000.
Pyrene	10,000.	38,000.	11,000.	42,000.	10,000.	38,000.
Triphenylene	20,000.	76,000.	7,000.	26,000.	14,000.	53,000.
Benz(a)anthracene	12,000.	45,000.	5,300.	20,000.	9,000.	34,000.
Chrysene	36,000.	140,000.	190,000.	72,000.	28,000.	110,000.
Benzo(e)pyrene	160.	610.	140.	530.	150.	570.
Benzo(a)pyrene	62.	240.	23.	87.	42.	160.
Benzo(g,h,i)perylene	62.	240.	63.	240.	62.	240.

TABLE B-4

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN EM-239-F

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	380,000.	1,400,000.	300,000.	1,100,000.	340,000.	1,300,000.
Anthracene	9,000.	34,000.	11,000.	42,000.	10,000.	38,000.
Fluoranthene	13,000.	49,000.	13,000.	49,000.	13,000.	49,000.
Pyrene	8,700.	33,000.	7,400.	28,000.	8,000.	30,000.
Triphenylene	4,000.	15,000.	4,900.	19,000.	4,400.	17,000.
Benz(a)anthracene	3,100.	12,000.	3,900.	15,000.	3,500.	13,000.
Chrysene	2,800.	11,000.	5,800.	22,000.	4,300.	16,000.
Benzo(e)pyrene	75.	280.	79.	300.	77.	290.
Benzo(a)pyrene	58.	220.	80.	300.	69.	260.
Benzo(g,h,i)perylene	29.	110.	31.	117.	30.	110.

TABLE B-5

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN EM-240-F

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	8,300.	31,000.	7,700.	29,000	8,000.	30,000.
Anthracene	180.	680.	210.	800.	200.	760.
Fluoranthene	140.	530.	170.	640.	160.	610.
Pyrene	51.	190.	54.	200.	52.	200.
Triphenylene	74.	280.	74.	280.	74.	280.
Benz(a)anthracene	55.	210.	56.	210.	56.	210.
Chrysene	83.	310.	83.	310.	83.	310.
Benzo(e)pyrene	9.0	34.	12.	45.	10.	38.
Benzo(a)pyrene	7.1	27.	7.7	29.	7.4	280.

TABLE B-6

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN EM-241-F

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	700,000.	2,700,000.	920,000.	3,500,000.	810,000.	3,100,000.
Anthracene	10,000.	380,000.	7,100.	27,000.	8,600.	33,000
Fluoranthene	14,000.	53,000.	18,000.	68,000.	16,000.	61,000.
Pyrene	12,000.	45,000.	17,000.	64,000.	14,000.	53,000.
Triphenylene	3,900.	15,000.	4,500.	17,000.	4,200.	16,000.
Benz(a)anthracene	3,200.	12,000.	3,500.	13,000.	3,400.	13,000.
Chrysene	5,600.	21,000.	6,800.	26.000	6,200.	24,000.
Benzo(e)pyrene	58.	220.	48.	180.	53.	200.
Benzo(a)pyrene	40.	150.	47.	180.	44.	170.
Benzo(g,h,i)perylene	13.	49.	22.	83.	18.	68.

TABLE B-7

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN EM-242-F

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	200,000.	760,000.	220,000.	830,000.	210,000.	800,000.
Anthracene	900.	3,400.	2,500.	9,500.	1,700.	6,400.
Fluoranthene	4,600.	17,000.	5,700.	22,000.	5,200.	20,000.
Pyrene	2,000.	7,600.	2,100.	8,000.	2,000.	7,600.
Triphenylene	1,700.	6,400.	1,600.	6,100.	1,600.	6,100.
Benz(a)anthracene	600.	2,300.	600.	2,300.	600.	2,300.
Chrysene	1,400.	5,300.	1,500.	5,700.	1,400.	5,300.
Benzo(e)pyrene	17.	64.	17.	64.	17.	64.
Benzo(a)pyrene	20.	76.	21.	80.	20.	76.

TABLE B-8

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN COUCH #2

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	510,000.	1,900,000.	570,000.	2,200,000.	540,000.	2,000,000.
Anthracene	3,200.	12,000.	2,600.	9,900	2,900.	11,000.
Fluoranthene	19,000.	72,000.	21,000.	80,000.	20,000.	76,000.
Pyrene	26,000.	99,000.	35,000.	130,000.	31,000.	120,000.
Triphenylene	10,000.	38,000.	11,000.	42,000.	11,000.	42,000.
Benz(a)anthracene	8,100.	31,000.	6,800.	26,000.	7,500.	28,000.
Chrysene	14,000.	53,000.	14,000.	53,000.	14,000.	53,000.
Benzo(e)pyrene	130.	490.	170.	640.	150.	570.
Benzo(a)pyrene	79.	300.	98.	370.	88.	330.
Benzo(g,h,i)perylene	43.	160.	15.	57.	29.	110.

TABLE B-9

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN COUCH #5A

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	6,000.	23,000.	3,900.	15,000.	5,000.	19,000.
Anthracene	330.	1,200.	290.	1,100.	310.	1,200.
Fluoranthene	1,900.	7,200.	1,700.	6,500.	1,800.	6,800.
Pyrene	6,600.	25,000.	4,500.	17,000.	5,600.	21,000.
Triphenylene	1,500.	5,700.	1,600.	6,100.	1,600.	6,100.
Benz(a)anthracene	660.	2,500.	700.	2,700.	680.	2,600.
Chrysene	1,200.	4,500.	1,300.	4,900.	1,200.	4,500.
Benzo(e)pyrene	380.	1,400.	380.	1,400.	380.	1,400.
Benzo(a)pyrene	210.	800.	210.	800.	210.	800.
Benzo(g,h,i)perylene	6.7	25.	8.9	34.	7.8	30.

TABLE B-10

CONCENTRATION OF POLYNUCLEAR AROMATIC HYDROCARBONS IN COUCH #5B

Compound	Concentration					
	Analysis I		Analysis II		Average	
	ppb	µg/gal	ppb	µg/gal	ppb	µg/gal
Phenanthrene	8,500.	32,000.	13,000.	49,000.	11,000.	42,000.
Anthracene	250.	950.	360.	1,400.	300.	1,200.
Fluoranthene	2,000.	7,600.	2,100.	8,000.	2,000.	7,800.
Pyrene	3,100.	12,000.	2,200.	8,300.	2,600.	10,000.
Triphenylene	1,100.	4,200.	1,200.	4,500.	1,200.	4,500.
Benz(a)anthracene	520.	2,000.	540.	2,000.	530.	2,000.
Chrysene	1,100.	4,200.	1,200.	4,500.	1,200.	4,500.
Benzo(e)pyrene	320.	1,200.	320.	1,200.	320.	1,200.
Benzo(a)pyrene	190.	720.	190.	720.	190.	720.
Benzo(g,h,i)perylene	8.8	33.	11.	42.	9.9	38.